PCT/AU03/01313

Patent Office
Canberra

I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002951838 for a patent by UNISEARCH LIMITED as filed on 08 October 2002.

WITNESS my hand this
Twenty-second day of October 2003

J. Billingsley

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

AUSTRALIA

Patents Act 1990

Unisearch Limited

PROVISIONAL SPECIFICATION

Invention Title:

Method of preparation for polycrystalline semiconductor films

The invention is described in the following statement:

METHOD OF PREPARATION FOR POLYCRYSTALLINE SEMICONDUCTOR FILMS

Introduction

The present invention relates generally to the formation of thin semiconductor films for electronic device fabrication, and in particular the invention provides an improved method for the formation of thin *polycrystalline* semiconductor films at low temperature. Throughout this text, *polycrystalline material* means that the material has an average crystal grain size of above 500 nm.

Background of the Invention

The formation of polycrystalline semiconductor films at low temperature on low-cost substrates (such as glass) using simple and fast processes is of interest for large-area electronics (flat panel displays, detectors, etc) and photovoltaics (thin-film solar cells). As the high melting point of semiconductors is a major obstacle for the formation of polycrystalline semiconductor films at low temperature, past experimental work dealt primarily with the fabrication of *nanocrystalline* (or, equivalently, microcrystalline) material. Such fine-grained (< 500 nm) material is inevitably of rather low electronic quality. An overview of nanocrystalline silicon materials is given in the 1998 book by Schropp and Zeman. One approach for the fabrication of nanocrystalline materials is hydrogen-diluted plasma-enhanced chemical vapour deposition (PECVD) at a temperature in the range 200-600°C, whereby the hydrogen is beneficial for both the semiconductor growth process and the passivation of dangling crystallographic bonds within grains and at grain boundaries. A drawback of the hydrogen-diluted PECVD approach with regard to the manufacture of devices that require a rather thick semiconductor film (such as crystalline silicon solar cells) is the low semiconductor deposition rate (much less than 1 nm/s in the case of Si).

The present invention deals with polycrystalline semiconductor materials made at low temperature (< 650°C). Compared to nanocrystalline material, polycrystalline material usually has a much better electronic quality. Methods for the low-temperature fabrication of polycrystalline semiconductor films include solid-phase crystallisation of amorphous semiconductor material (see,

for instance, the 1996 paper by Matsuyama et al.), solution growth (see, for instance, the 1994 paper by Shi et al.), laser-induced crystallisation of amorphous semiconductor material (see, for instance, the 1996 paper by Im and Sposili), and metal-induced (or, equivalently, metal-mediated) crystallisation of amorphous semiconductor material (see the 1977 paper by Majni and Ottaviani [Al-Si], the 1998 paper by Nast et al. [Al-Si] and the 2000 patent to Joo et al. [Ni-Si]). For optimum results on foreign substrates, the preparation of polycrystalline material often involves a preliminary step that creates a thin polycrystalline *seed layer* on the substrate, whereby the electronic quality of this seed layer is not critical. Such seed layers can, in principle, be prepared by each of the methods mentioned above.

The metal-induced crystallisation (MIC) process of amorphous semiconductor material as developed at the University of New South Wales (UNSW) and disclosed (see the 2000 paper by Nast and Hartmann for the Si-Al system on glass) is simple and fast and hence has significant industrial appeal. The metal and semiconductor must be chosen such that they can form a eutectic system, enabling crystallisation at low temperature without the formation of metal silicide. However, with respect to using the resulting polycrystalline semiconductor film for the fabrication of electronic devices or as seed layer, a significant problem of the MIC-prepared continuous polycrystalline semiconductor film is the fact that it is covered by an overlayer consisting of metal and semiconductor inclusions, whereby additionally an interfacial metal oxide (or metal hydroxide) film exists between the polycrystalline semiconductor film and the overlayer.

The low-temperature (< 650°C) formation of a continuous polycrystalline semiconductor film on a supporting substrate by means of metal-induced crystallisation of amorphous films of the same semiconductor material is generally known in the prior art. The process using crystalline silicon wafers as substrate and Al as metal is, for example, described in the 1977 paper by Majni and Ottaviani. The process for the Si-Al system and glass as substrate is described in the 2000 paper by Nast et al. and the 2002 paper by Widenborg and Aberle, and is schematically shown in Figures 1 and 2. The process consists of depositing (e.g., by vacuum evaporation) about 500 nm of metal 11 onto the substrate 10, followed by a process (e.g. native metal oxide growth) that forms a metal oxide or metal hydroxide film 12 on the metal surface, followed by the deposition (e.g., by sputtering) of an amorphous semiconductor

film 13 slightly thicker than the metal layer 11 onto the metal oxide (hydroxide) surface 12 (Figure 1). During a subsequent anneal at a temperature below 650°C a layer exchange occurs, producing a thin (~500 nm), fully crystallised, continuous polycrystalline semiconductor film 14 on the substrate. As shown in Figure 2, the continuous polycrystalline semiconductor film 14 is covered by a thin (~500 nm) overlayer 15 consisting of metal 16 and some semiconductor inclusions 17. In addition, there is a thin (~30 nm) porous interfacial film 18 consisting of metal oxide and/or metal hydroxide between the polycrystalline semiconductor film 14 and the overlayer 15. The porous interfacial film 18 varies in thickness laterally and may contain a few pinpoint areas with direct contact between the semiconductor layer 14 and the inclusions 17. The semiconductor inclusions 17 are strongly connected to the underlying porous interfacial metal oxide (hydroxide) film 18. The continuous polycrystalline semiconductor film 14 is of primary interest for device fabrication (such as thin-film transistors) or seed layer applications, and hence the metal oxide (hydroxide) interfacial film 18 and the metal+semiconductor overlayer 15 must be removed by a suitable processing sequence without significantly thinning or damaging the underlying polycrystalline semiconductor film 14. A conceivable way to achieve this consists in using a method that uniformly removes the metal+semiconductor overlayer. This is a very difficult task because, in general, the etching rates for the different components of a composite material, such as the overlayer 15, are not identical. A possible candidate for this purpose is plasma ion etching. For the Si-Al system, we have tested the use of an argon plasma, however, these efforts were unsuccessful due to a very low etching rate. Another possible candidate is reactive ion etching with a chlorine plasma. This process, however, appears unattractive due to its technical complexities, as discussed on pages 559 to 564 in the 1986 book by Wolf and Tauber.

Given the difficulties with the above non-selective methods, a *selective* approach appears interesting. One such attempt that has been investigated at UNSW (and elsewhere) and disclosed (see the 1998 paper by Nast et al. or the 2001 paper by Niira et al.) is the wet-chemical removal of the metal. However, because this does not remove the semiconductor inclusions, this process creates a very rough polycrystalline semiconductor surface that leads to numerous (and virtually insurmountable) problems during subsequent device processing. The creation of this rough surface will very likely have detrimental

effects on the electrical performance of the devices or, in the case of seed layer applications, on the structural properties of a subsequently grown polycrystalline semiconductor film.

Hence, although the prior art discloses (see the 1998 by Nast et al. and 2001 paper by Niira et al.) the formation of a continuous polycrystalline semiconductor film with *rough* surface (i.e, the film has a non-uniform thickness) at low temperature on a substrate by means of metal-induced crystallisation of amorphous semiconductor material, there is no disclosure of fabrication of a continuous polycrystalline film with *smooth* surface and uniform thickness based on removing the metal oxide (hydroxide) interfacial film and subsequent lift-off of the semiconductor inclusions.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Summary of the Invention

The present invention consists in a method of preparing polycrystalline semiconductor films fabricated at low temperature (< 650°C) on supporting substrates, comprising:

Forming a metal film onto a target surface on which the polycrystalline semiconductor film is to be formed, over the substrate;

Forming a layer of metal oxide or metal hydroxide on a surface of the metal;

Forming a layer of an amorphous semiconductor material over a surface of the metal oxide or metal hydroxide;

Heating the entire sample at a temperature at which the semiconductor layer is absorbed into the metal layer and deposited onto the target surface by metal-induced crystallisation as a polycrystalline layer, whereby the metal is left

as an overlayer covering the deposited polycrystalline layer, with semiconductor inclusions in the metal layer, and a porous interfacial metal oxide or metal hydroxide film between the polycrystalline semiconductor film and the overlayer;

Removal of the metal in the overlayer and the interfacial film with an etch, without significantly thinning the underlying polycrystalline semiconductor layer.

Removal of the semiconductor inclusions from the surface of the polycrystalline semiconductor layer by a lift-off process.

In some embodiments of the invention the target surface is formed on a preliminary layer deposited over the substrate, however the target surface may also be a surface of the substrate on which the process of the present invention is performed directly.

In various embodiments of the invention the substrate is a material selected from the group comprising sapphire, quartz, glass (float, borosilicate and other types), crystalline silicon, crystalline germanium, metal graphite ceramics, plastics and polymers.

Embodiments of the invention may make use of a semiconductor material selected from the group comprising silicon and germanium.

The metal used in various embodiments is selected such that the metal forms a eutectic solution with the selected semiconductor. For example the metal may be selected from the group of metals comprising Be, Al, Zn Ga, Ag, Cd, In, Sn, Sb and Au.

The metal and metal oxide or hydroxide etch is preferably performed with a phosphoric acid solution, using a 100% solution of 70% phosphoric acid, at about 110°C for about 10 minutes. Weaker solutions of phosphoric acid may also be used with a corresponding increase in etching time. Alternatively the etch may also be performed with other acids such as hydrochloric acid.

Embodiments of the invention may make use of a lift-off process selected from the group comprising an acoustic treatment in de-ionized water or other solutions, a brush scrubbing process, or a hydrodynamic jet process.

Preferably the method will include a further processing step wherein, upon completion of the lift-off step, a uniform surface treatment is performed to improve the surface finish of the sample prior to subsequent use of the semiconductor film for device fabrication or as a seed layer. Examples the uniform surface treatment may be selected from the group comprising a KOH

etch, a NaOH etch, a HF/HNO_3 etch, a H_3PO_4 etch, an argon plasma etch, or a combination of these.

Brief Description of the Drawings

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 (Prior Art) illustrates a first step in fabrication of a thin-film polycrystalline layer where a substrate has a layer of metal formed over it, then a metal oxide or metal hydroxide formed on the metal, followed by a layer of amorphous semiconductor material as a precursor for growth of a polycrystalline film by metal-induced crystallisation;

Figure 2 (Prior Art) illustrates the sample of Figure 1 after a layer exchange has occurred, leaving a polycrystalline layer covered by a metal layer with semiconductor inclusions. Additionally, an interfacial oxide (hydroxide) layer exists between the polycrystalline layer and the metal plus semiconductor overlayer;

Figure 3 (Prior Art) illustrates the samples of Figure 1 and 2 after the metal has been removed, leaving a continuous polycrystalline layer covered by a continuous layer of metal oxide (hydroxide), and with semiconductor inclusions adhering strongly to the metal oxide (hydroxide) surface.

Figure 4 illustrates the sample of Figure 3 after a metal oxide (hydroxide) etch which removed the metal oxide (hydroxide) film from the uncovered surface of the polycrystalline semiconductor layer *and also* between the semiconductor inclusions and the semiconductor film according to the present invention; and

Figure 5 illustrates the sample of Figure 4 after a lift-off step according to the present invention.

Detailed Description of an Embodiment of the Invention

Starting point for embodiments of the present invention is the sample structure shown in Figure 2. The continuous polycrystalline semiconductor film 14 on the substrate 10 was fabricated at low temperature (below 650°C) by means of metal-induced crystallisation of an amorphous film of the same semiconductor material, as disclosed in the literature (see, for example, the 1998 paper by Nast et al. and the 2002 paper by Widenborg and Aberle). The metal and semiconductor must be chosen such that they can form an eutectic

system, and for the purpose of this example silicon and aluminium are used, however it will be recognised that other semiconductor/metal combinations can be selected from the groups of semiconductors and metal given above. As shown in Figure 2, the continuous polycrystalline semiconductor film 14 is covered by a thin (~500 nm) overlayer 15 consisting of metal 16 and some semiconductor inclusions 17. In addition, there is a thin (~30 nm) porous interfacial film 18 consisting of metal oxide (hydroxide) between the polycrystalline semiconductor film 14 and the overlayer 15. The porous interfacial film 18 varies in thickness and may contain a few pinpoint areas with direct contact between the semiconductor layer 14 and the inclusions 17. The semiconductor inclusions 17 are strongly connected to the underlying interfacial metal oxide (hydroxide) film 18. Figure 3 illustrates the sample of Figure 2 after the metal 16 has been removed (known in prior art), leaving a polycrystalline layer 14 covered by a metal oxide (hydroxide) film 18 with semiconductor inclusions 17 adhering strongly to the metal oxide (hydroxide) surface 18.

The removal of the metal oxide (hydroxide) layer 18 (see Figure 4) between the polycrystalline layer 14 and semiconductor inclusions 17 significantly decreases the adhesion strength between the semiconductor inclusions 17 and the polycrystalline layer 14, enabling a following lift-off process regarding the semiconductor inclusions. For the Al-Si system, a suitable metal oxide (hydroxide) etching method is, for example, a phosphoric acid etch, using a 100% solution of 70% phosphoric acid, at 110°C for 10 minutes. Weaker solutions of phosphoric acid may also be used with a corresponding increase in etching time. Alternatively the etch may also be performed with other acids such as hydrochloric acid. This etch removes the aluminium oxide (hydroxide) layer 18 without significantly etching the underlying polycrystalline silicon layer 14, and hereby significantly decreases the adhesion of the semiconductor inclusions 17.

Next, a cleaning sequence is used which effects a lift-off of the semiconductor inclusions 17, an example being ultrasonic treatment in deionized water of the sample of Figure 4, to thereby produce a continuous polycrystalline semiconductor film with uniform thickness on the substrate. An additional, optional, processing step is a uniform surface treatment that improves the surface finish of the sample prior to subsequent device fabrication or use as a seed layer. Figure 5 shows a schematic representation of a sample prepared in accordance with an embodiment of the present invention.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Dated this eighth day of October 2002

Unisearch Limited
Patent Attorneys for the Applicant:

F B RICE & CO

REFERENCES

Majni and Ottaviani, "Large-area uniform growth of <100> Si through Al film by solid epitaxy", Applied Physics Letters 31, pp. 125-126 (July 1977).

Wolf and Tauber, "Silicon processing for the VLSI era", Vol. 1, Lattice Press, CA, USA (1986).

Shi et al., "Solution growth of polycrystalline silicon on glass at low temperatures", Proceedings First World Conference on Photovoltaic Energy Conversion, Hawaii, pp. 1579-1582 (Dec. 1994) (IEEE, New York, 1995).

Im and Sposili, "Sequential lateral solidification of thin silicon films on SiO_2", Applied Physics Letters 69, pp. 2864-2866 (1996).

Matsuyama et al., "High-quality polycrystalline silicon thin film prepared by a solid phase crystallization method", Journal of Non-Crystalline Solids 198-200, pp 940-944 (1996).

Schropp and Zeman, "Amorphous and microcrystalline silicon solar cells", Kluwer Academic Publishers, Dordrecht (1998).

Nast et al., "Aluminum-induced crystallization of amorphous silicon on glass substrates above and below the eutectic temperature", Applied Physics Letters 73, pp. 3214-3216 (Nov. 1998).

Nast and Hartmann, "Influence of interface and Al structure on layer exchange during aluminum-induced crystallization of amorphous silicon", Journal of Applied Physics 88, pp. 716-724 (July 2000).

Niira et al., "Thin film poly-Si formation for solar cells by flux method and Cat-CVD method", Solar Energy Materials & Solar Cells 69, pp. 107-114 (Sep. 2001).

Widenborg and Aberle, "Surface morphology of poly-Si films made by aluminium-induced crystallisation on glass substrates" Journal of Crystal Growth 242, pp. 270-282 (July 2002).

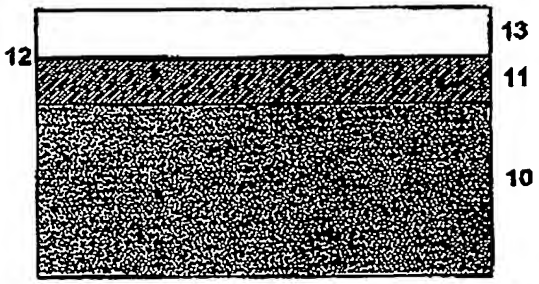

Figure 1
(Prior Art)

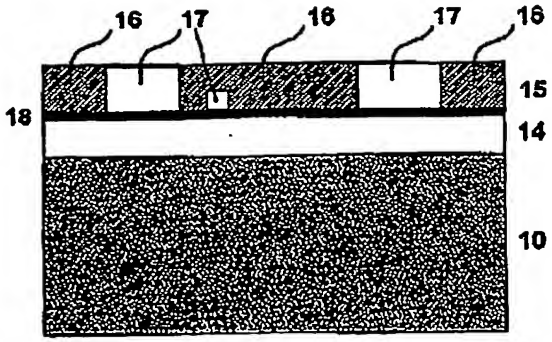

Figure 2
(Prior Art)

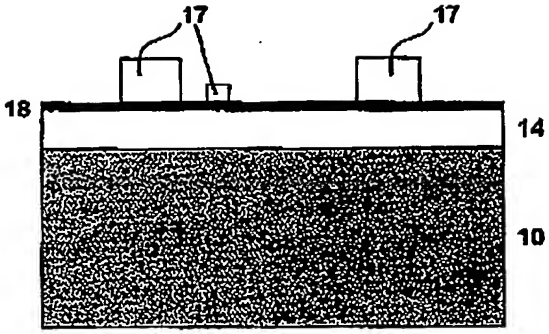

Figure 3
(Prior Art)

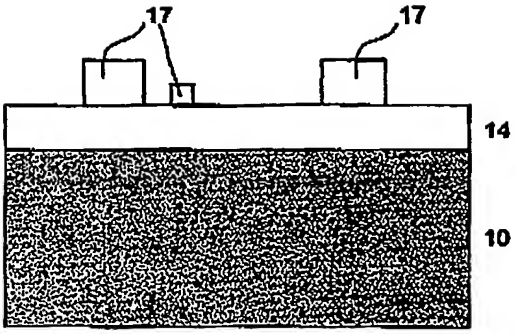

Figure 4

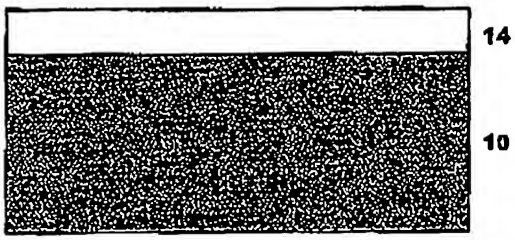

Figure 5